

# Formation and Characterization of Cellulose Films from a Liquid Crystalline Solution of Cellulose in Ammonia/Ammonium Thiocyanate

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## Synopsis

Films were cast from liquid crystalline solutions of cellulose in an ammonia ( $\text{NH}_3$ )/ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) solvent. Microscopic examination of the cellulose liquid crystalline solutions used for the film formation exhibited the so-called conjugated phase. It displayed a fingerprint and a uniformly dispersed highly birefringent pattern. Without additives, the films made from these liquid crystalline solutions are clear, flexible, and have high strength comparable to commercial Cellophane® films. The infrared crystallinity index of the film was somewhat higher than that of other cellulose II materials.

## INTRODUCTION

Over the past several years, a variety of new solvents has been investigated for the dissolution of cellulose and cellulose derivatives. Of particular interest are those for which the formation of a polymeric liquid crystalline state has been reported.<sup>1,2</sup> Previous studies in this laboratory have shown that a lyotropic mesophase can be obtained by dissolving cellulose above a certain minimum concentration in the ammonia ( $\text{NH}_3$ )/ammonium thiocyanate ( $\text{NH}_4\text{SCN}$ ) system.<sup>3</sup> This minimum value depends upon several factors, such as cellulose source and DP and solvent composition. In the same system, cholesteric-nematic phase transformations were observed with variation of the solvent composition.<sup>4</sup> In this paper, the preparation and properties of cellulose films from the liquid crystalline solutions are discussed.

## EXPERIMENTAL

### Materials

Cellulose powder (DP 210), CC-41 microgranular grade, was obtained from Whatman Chemical Ltd., and used without further drying.

Ammonium thiocyanate from Ventron Corp. was purified by recrystallization from methanol. The solvent composition used consisted of 25%  $\text{NH}_3$  and 75%  $\text{NH}_4\text{SCN}$  by weight and was prepared by condensing  $\text{NH}_3$  to a predetermined weight with a known amount of  $\text{NH}_4\text{SCN}$ .

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### Preparation of Cellulose Liquid Crystalline Solutions

A known amount of cellulose in 20 mL solvent was placed in a container equipped with a tight cap. After mixing thoroughly by stirring, the resulting cellulose slurry was placed in a dry-ice bath for 10 h or longer, followed by warming to room temperature while being mechanically stirred. Further details on the method of cellulose dissolution in the solvent are given in an earlier article.<sup>3</sup>

Samples for fracture surface examination were prepared by coagulating the cellulose in a system essentially devoid of shear. This was done in an attempt to detect in the solid any structure inherent to the cellulose solution. A cellulose solution in  $\text{NH}_3/\text{NH}_4\text{SCN}$  was placed in a beaker. The cellulose was coagulated by allowing a slow stream of water to flow into the beaker over *ca.* 30 min. The precipitate was dried at 120°C for 2 h. The solid cellulose was then fractured in liquid nitrogen.

### Preparation of Cellulose Films

A portion of 20% (w/v) solution of cellulose in the solvent was poured on to a glass plate. A glass rod was carefully pushed over the solution to form a thin film. The thickness of the film was controlled by sticking two lengths of Scotch® tape, one over the other, parallel to each other along the sides of the glass plate. The glass plate with the cellulose solution was then placed in a methanol coagulation bath for approximately 15 min, followed by washing in running water for 30 min to remove all the  $\text{NH}_4\text{SCN}$  salt. The presence or absence of thiocyanate salt in the film can be shown by treatment of the retrieved cellulose with a strongly acidified 1% solution of  $\text{FeCl}_3$ . A trace amount of thiocyanate will show a bright red color due to the formation of the complex,  $\text{Fe}(\text{CN})_6^{-3}$ .<sup>5</sup> Absence of the salt was also verified using infrared and elemental analysis for nitrogen and sulfur.

The coagulated film was lifted from the glass plate and mounted on a square frame. Further treatment included (i) air drying, (ii) drying in an oven at 70°C for 30 min, or (iii) soaking in a solution of 10% glycerol in methanol or 10% glycerol in water for 24 h, followed by air drying.

### Measurements

All optical observations were made on a Vickers Optical Microscope equipped with crossed polars. Photographs of fracture surfaces made in liquid nitrogen were taken using an ISI-40 scanning electron microscope (SEM). The samples were pretreated with a gold-palladium alloy. Infrared spectra were obtained by using a Perkin-Elmer 281-B Infrared Spectrophotometer. Wide angle X-ray diffraction photographs were taken with a Siemens X-ray system. The radiation used was Nickel filtered  $\text{CuK}_\alpha$  of wavelength 1.542 Å, with a beam power of 600 W. The tensile properties of the cellulose films were determined with an Instron Tensile Tester (Instron Model 1123) following ASTM method D882-80A. The specimens were preconditioned for one day and measured under standard conditions at 22°C and 65% RH. The force to propagate a tear across a film specimen was measured at 22°C and 65% RH using an Instron Tester (Model 1123) as described in ASTM method D1938-67. The moisture regain

of the retrieved cellulose was determined by Karl-Fischer method as described in ASTM D1348-61. The density of the films was measured at  $23^\circ\text{C}$  in a density gradient column (ASTM D1505-68) prepared from a  $\text{CCl}_4$ -toluene mixture. The column was calibrated using calibration floats having densities ranging from 1.450 to 1.590.

## RESULTS AND DISCUSSION

The fracture surfaces of the samples prepared from the liquid crystalline solutions exhibit surface patterns (Fig. 1). The patterns suggest that the samples consist of multidomains containing cellulose molecules aligned with each other within each domain. It is believed that the molecular orientation in each domain originated from the inherent molecular orientations in the liquid crystalline solution consisting of stacks of polydomains.<sup>6</sup>

The cellulose films made from liquid crystalline solutions of cellulose/ $\text{NH}_3$ / $\text{NH}_4\text{SCN}$  are transparent and water-clear. They show birefringence when viewed under a polarizing microscope. Using a quartz compensator, the birefringence was estimated to be 0.003. The fracture surface of the film edge (Fig. 2) seems to indicate that the film has a bilayered structure. The thinner upper layer of the film (6% of total thickness) formed on the side sheared by the glass rod during the formation of the film. The molecular orientation of the upper layer seems higher than that of the lower layer. This might have resulted from shear-induced molecular orientation. Higher molecular orientation in the upper layer may have led to a rapid coagulation rate relative to the lower layer.

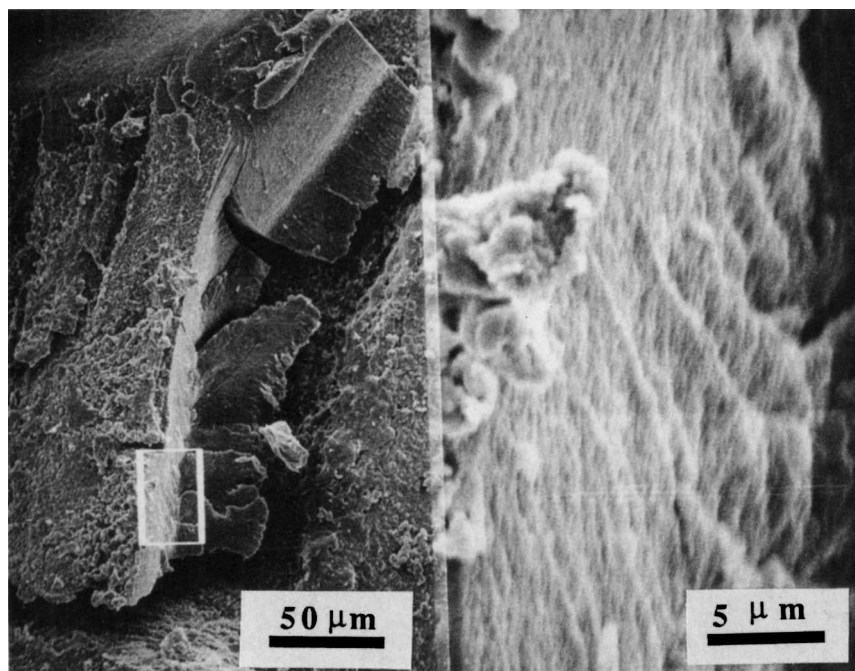


Fig. 1. Fracture surface of solidified sample prepared from liquid crystalline solution.

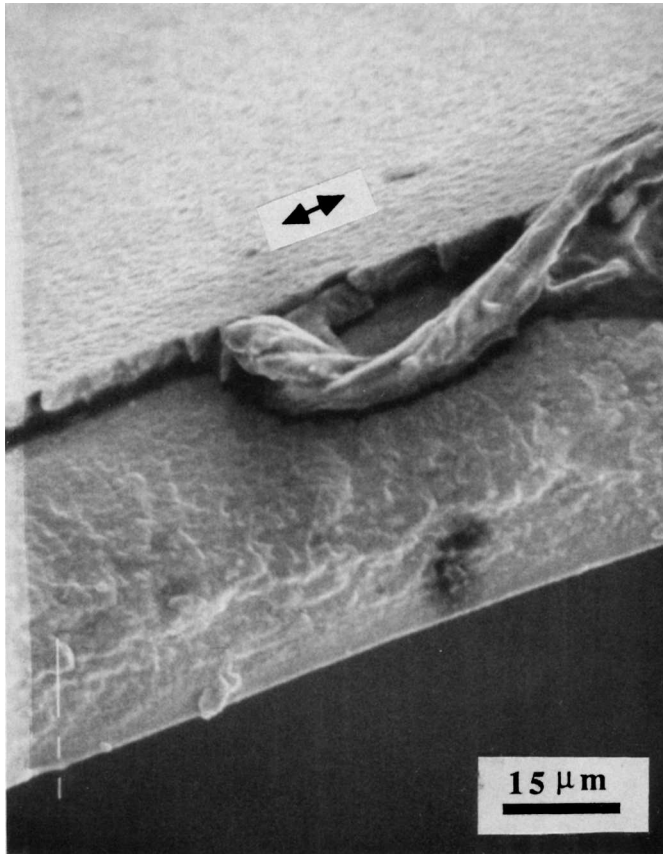


Fig. 2. Fracture surface of film edge;  $\rightleftarrows$ , shear direction.

This results in the observed porous upper layer and the consequent skin-core structure of the film. The birefringence of the films is believed to originate from the thinner, oriented upper portion.<sup>7,8</sup> Considering the limited depth of the shear effect, finding appropriate conditions (viscosity, anisotropy of the solution, etc.) will be important to control the orientation of the molecules throughout the film.

The retrieved films were proved free of  $\text{NH}_4\text{SCN}$  by using  $\text{FeCl}_3$  treatment, elemental analysis, and infrared spectroscopy. The infrared spectra shown in Figure 3 revealed no evidence of either chemical changes or derivatization of the retrieved cellulose.

Figure 4 is a wide-angle X-ray diffraction photograph taken on a multilayered thin film. The inner strong reflection of the X-ray pattern is assigned to (200), and the outer two reflections correspond to (004) and (006).<sup>9</sup> The Debye rings indicate that the cellulose crystals are oriented at random with respect to the axis perpendicular to the film surface. These observations suggest that the (0k0) planes of the cellulose crystal have uniplanar orientation parallel to the film surface according to the nomenclature of Hefelfinger and Burton.<sup>10</sup> From another X-ray study, it was found that the films cast from the cellulose/ $\text{NH}_3$ / $\text{NH}_4\text{SCN}$  system have the cellulose II crystalline structure.<sup>11</sup>

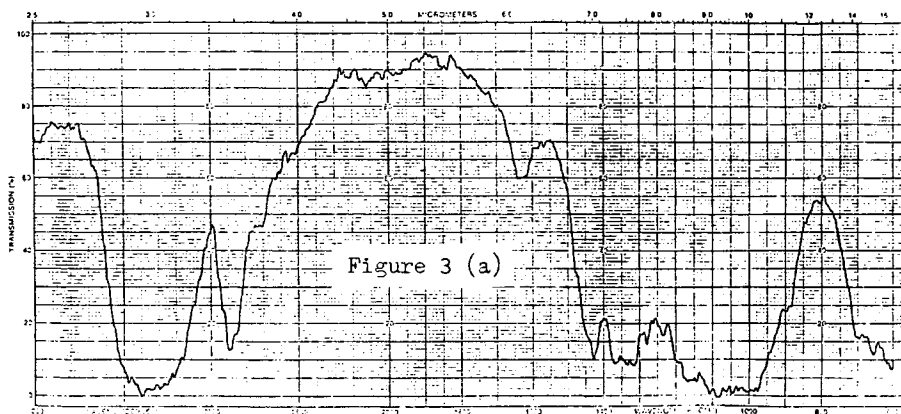


Figure 3 (a)

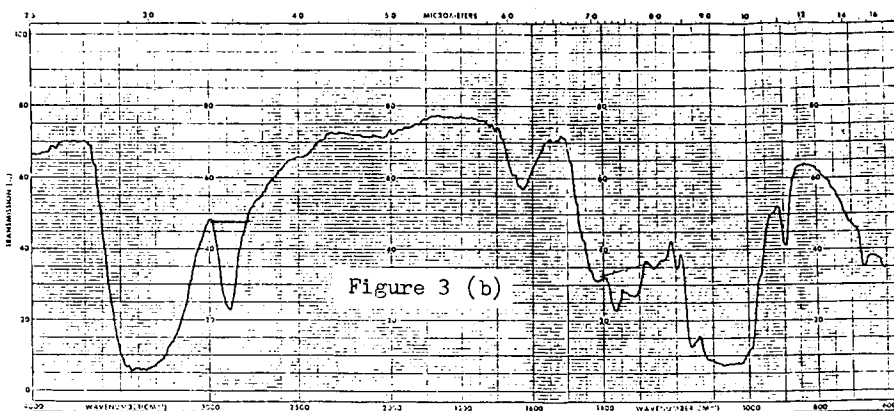


Figure 3 (b)

Fig. 3. Infrared spectra of cellulose: (a) Cellulose powder before dissolution, KBr pellet; (b) Cellulose film retrieved from liquid crystalline solution of cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$ .

Moisture regain values of the retrieved cellulose films from  $\text{NH}_3/\text{NH}_4\text{SCN}$  are 7–8% at 22°C and 65% RH (Table I). Since water molecules do not penetrate the crystalline regions of cellulose, the moisture must be absorbed in the less ordered regions and on the surface of crystallites.<sup>12,13</sup> The moisture regain of the retrieved films is lower than that of viscose fiber and is the same as that of cotton. Cellophane® is normally finished with a water-proofing agent.<sup>14</sup> Considering these facts, the low values of moisture regain also suggest a rather highly ordered structure of the cellulose films.

The ratio of absorbance at  $1372\text{ cm}^{-1}$  (C–H bending) to the absorbance at  $2900\text{ cm}^{-1}$  (C–H stretching) in the infrared spectrum, proposed by Nelson and O'Connor, can be used for measuring the crystallinity in cellulose materials.<sup>15</sup> The average value infrared crystallinity index ( $a_{1372}/a_{2900}$ ) calculated from spectra as shown in Figure 3 was found to be *ca.* 0.5 (see Table I), which is in the range of mercerized cotton as reported by Nelson and O'Connor. Table I shows that crystalline index is larger than that of any other cellulose II ma-

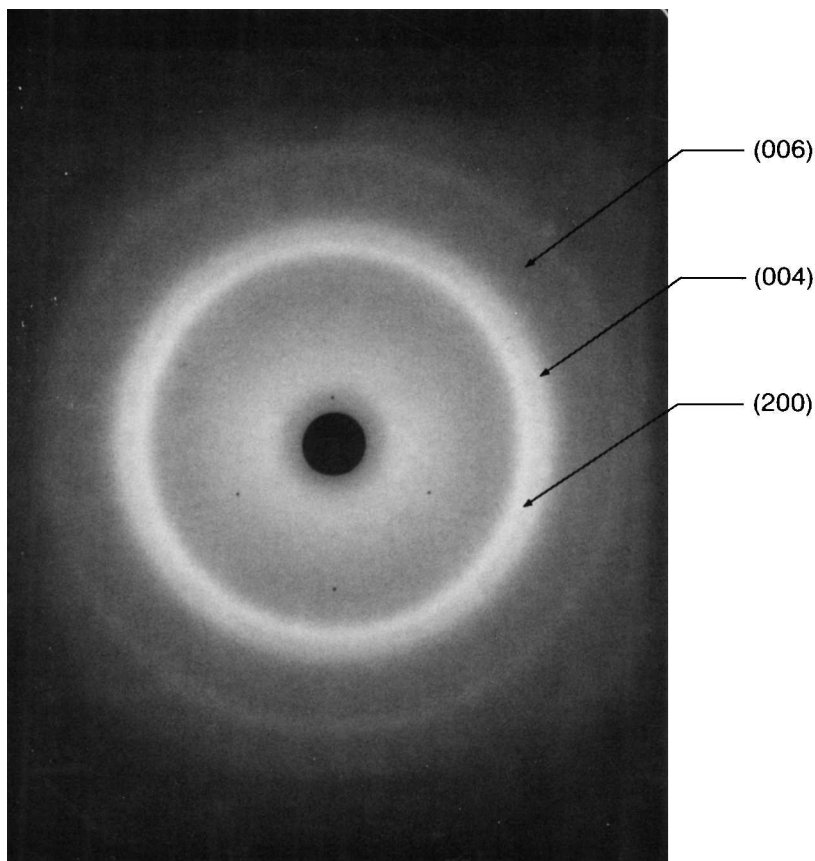


Fig. 4. Wide-angle X-ray photograph of cellulose film from liquid crystalline solution of cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$ .

terials. The unexpectedly low density of the retrieved film (Table II) at this stage of development can not be unequivocally explained. It could result from an inherent situation or, basically, simply from voids or bubbles in the cellulose film.

Table II compares the physical properties of films derived from cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$  with a commercial film. These data show that the films from liquid crystalline solutions of cellulose in the  $\text{NH}_3/\text{NH}_4\text{SCN}$  solvent and Cellophane<sup>®</sup> seem to have similar tensile properties as suggested by their respective close values of tensile strength and modulus of elasticity. The elongation was found to be 5–8% for the cellulose films, compared to 17–21% for the commercial films. The difference might be caused by (i) the properties peculiar to cellulose films derived from the anisotropic  $\text{NH}_3/\text{NH}_4\text{SCN}$  solution, and crystallinity, and by (ii) the presence of softeners or plasticizers in the commercial films. Experimental results have shown that the elongation of cellulosic films from  $\text{NH}_3/\text{NH}_4\text{SCN}$  can increase three times after treating with 10% glycerol solutions.

Heat treatment can have a positive effect on the tensile properties of polymeric products. In Table II, however, the results of a few preliminary mild heat

TABLE I  
Infrared Crystallinity Index ( $a_{1372 \text{ cm}^{-1}}/a_{2900 \text{ cm}^{-1}}$ ) and Moisture Regain Measured  
for Various Types of Cellulosic Materials

Cellulose source	Infrared crystallinity index ( $a_{1372 \text{ cm}^{-1}}/a_{2900 \text{ cm}^{-1}}$ )	Moisture regain (%) <sup>a</sup>	Ref.
Cotton	0.62	7-8	16, 17
Pulp	0.49	—	17
Viscose fiber	0.41	13	17, 18
Protofiber	0.18	—	17
Cellulose/NH <sub>3</sub> /NH <sub>4</sub> SCN fiber (spun from isotropic solution)	0.44	—	17
Cellophane (duPont made)	0.23	7-8	
Cellulose/NH <sub>3</sub> /NH <sub>4</sub> SCN film (cast from liquid crystalline solution)	0.50	7-8	

<sup>a</sup> Tested at 22°C and 65% RH.

treatment experiments caused little or no changes. But more recent experiments, heating the films at higher temperatures in ethylene glycol, appear to be very encouraging.

The retrieved cellulose films show essentially balanced behavior in the two directions parallel and normal to the shear direction. The respective values of the ratio of the former to the latter directions for the tensile strength and modulus are both only 1.2, indicating that there is relatively little preferred

TABLE II  
Physical Properties of Cellulose Films<sup>a</sup>

	Films from cellulose/NH <sub>3</sub> /NH <sub>4</sub> SCN					
	Parallel to shear direction		Normal to shear direction		Cellophane (from duPont)	Literature
	Air dry	Oven dry (70°C, 30 min)	Air dry	Oven dry (70°C, 30 min)		
Elongation (%)	7-8	7-8	5-6	5-6	17-21	10-50
Tensile strength						
Mpa	75.8-82.7	89.6-96.5	65.5-69.0	75.8-82.7	82.7-96.5	49.2-126.5
× 10 <sup>-3</sup> Psi	11-12	13-14	9.5-10	11-12	12-14	7.1-18.4
Elastic modulus						
Mpa	4482-4826	4826-5516	3792-4137	4137-4482	3447-4137	3450
× 10 <sup>-5</sup> Psi	6.5-7	7-8	5.5-6	6-6.5	5-6	5
Tear strength						
× 10 <sup>2</sup> g/mil	5-6	5-6	5-6	5-6	5-6	2-20
Density (23°C) g/mL			1.484		1.495	1.4-1.5

<sup>a</sup> Tested at 22°C and 65% RH.

orientation in the films. This low ratio may be related to the nature of the cholesteric structure of the anisotropic solutions used and to the method of film formation.

### CONCLUSIONS

Films made from liquid crystalline solutions of cellulose/ $\text{NH}_3/\text{NH}_4\text{SCN}$ , without any additives, are clear, flexible, and have high strength comparable to Cellophane®. It is felt that their structure and, therefore, the physical properties can be further enhanced or modified by incorporating a plasticizer or softener or by using a continuous casting process followed possibly by heat treating.

It is encouraging at this early stage of development to consider that a solvent-spun cellulose fiber or film product can be made by a simpler and very likely less expensive process than the viscose process and whose properties approach those of a commercial product.

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